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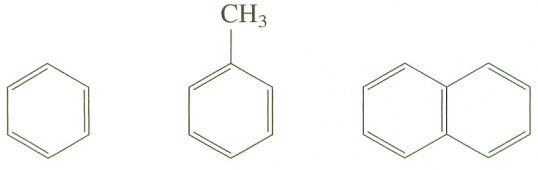
# Functional Groups and Nomenclature II

CHAPTER 12

THIS CHAPTER BEGINS where Chapter 5 left off and considers the nomenclature, physical properties, natural occurrences, and uses of the principal functional groups that were not discussed in Chapter 5. The nomenclature rules are extensions of those in Chapter 5, with different suffixes for the new functional groups. We will also see how compounds that have more than one functional group are named.

## 12.1 AROMATIC HYDROCARBONS

A complete definition of **aromatic compounds** must wait until Chapter 16. For the present we will define them as benzene and its substituted derivatives. They are also called **arenes.** These aromatic compounds have a six-membered ring with three conjugated double bonds. It is this cycle of conjugated double bonds that makes arenes special. Examples include the following:




Benzene Toluene Naphthalene

If you have spent much time in an organic laboratory, you are well aware that many organic compounds have rather strong (and sometimes disagreeable) odors. Aromatic compounds, however, tend to have more fragrant odors than other compounds. If you have a chance, compare the odor of toluene, for example, with that of cyclohexene. In fact, the term *aromatic* was originally given to

### MASTERING ORGANIC CHEMISTRY

- Naming Aromatic Compounds, Phenols, Aldehydes, Ketones, Carboxylic Acids, Acid Chlorides, Anhydrides, Esters, Amides, and Nitriles
- Drawing Structures of These Compounds from Their Names
- Recognizing the Common Functional Groups Containing Sulfur or Phosphorus
- Naming Compounds That Contain More Than One Functional Group
- Understanding How the Physical Properties of These Compounds Depend on the Functional Group That Is Present

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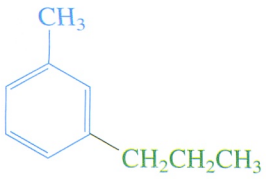
these compounds, even before their structures were known, because of their fragrant odors. Today, however, *aromatic* has evolved to mean something entirely different. To an organic chemist, an **aromatic compound** now means a compound that is especially stable because of its cycle of conjugated *p* orbitals. (The explanation for this special stabilization is provided in Chapter 16.)

Aromatic compounds are named by using benzene as the parent or root and designating the substituents attached to the ring in the same manner that is used to name groups attached to an alkane chain. (Cyclohexatriene is *never* used to name benzene, nor is it used in the names of any aromatic compounds.) Because of their stability, aromatic compounds are very common, and many were isolated in the very early days of organic chemistry. Many of the common names that were originally given to these compounds remain entrenched in the vocabulary of organic chemistry. For example, you will seldom hear methylbenzene referred to by this name; it will invariably be called toluene. Some of the more important of these common names will be introduced as the compounds are encountered.

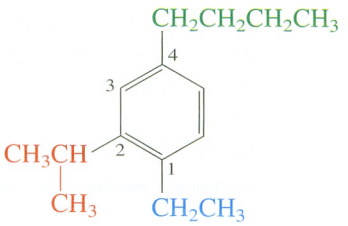
When several substituents are present on a benzene ring, the ring is numbered in the same manner as the rings of cycloalkanes—that is, so that the numbers for the substituents are as low as possible. In addition, some special terms are used with *disubstituted benzenes only*. Two substituents on adjacent carbons (positions 1 and 2) are said to be *ortho,* or *o*-. Two substituents on positions 1 and 3 are *meta,* or *m*-. And two substituents on positions 1 and 4 are *para,* or *p*-. Finally, if an alkyl group with six or more carbons is attached to a benzene ring, the compound is named as an alkane with a **phenyl** substituent. Some examples are as follows:




*m*-Propyltoluene
or 3-propyltoluene

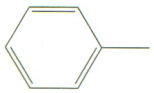
*p*-Dimethylbenzene
or 1,4-dimethylbenzene

(The common name for the dimethylbenzenes is xylene, so this is also called *p*-xylene.)



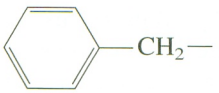

4-Butyl-1-ethyl-2-isopropylbenzene

(The numbering starts with the ethyl, so the numbers are 1, 2, and 4. If numbering started with the butyl, the numbers would be higher—1, 3, and 4.)

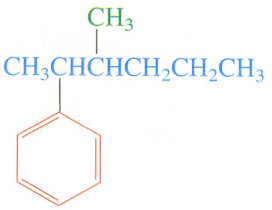


The phenyl group

(Recall that this group can be abbreviated as Ph in drawing structures.)




The benzyl group




3-Methyl-2-phenylhexane

(The larger or more highly substituted group, the alkyl group in this case, is chosen as the root.)

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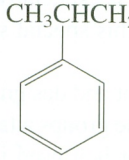
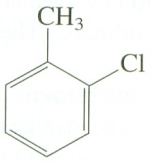
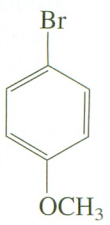
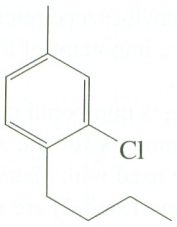
**PROBLEM 12.1**

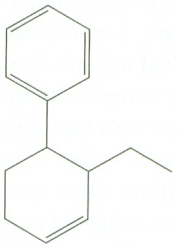
Provide names for these compounds:

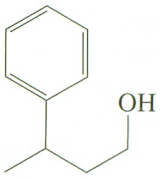
a) 


b) 


c) 


d) 


e) 

f) 


**PROBLEM 12.2**

Draw structures for these compounds:

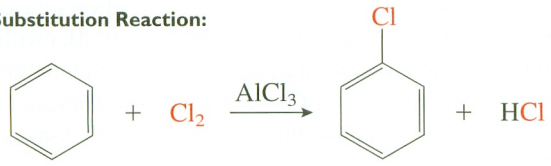
**a)** *p*-Ethyltoluene
**b)** *m*-Dichlorobenzene
**c)** 2-Phenyl-3-heptyne
**d)** 2-Bromo-1-chloro-3-pentylbenzene
**e)** *o*-Xylene
**f)** Benzyl methyl ether

Aromatic hydrocarbons are nonpolar, and their physical properties resemble those of alkanes of similar molecular mass. However, as was the case with cycloalkanes, the symmetrical shapes of many aromatic hydrocarbons often result in higher melting points. For example, the melting and boiling points of benzene are nearly identical to those of cyclohexane. (Recall that cyclohexane melts at considerably higher temperatures than does hexane.) As expected, a mixture of benzene and water forms two layers, with benzene as the upper layer.

On initial inspection, aromatic compounds might be expected to resemble alkenes in their chemical reactions. However, their reactions are dramatically different. Aromatic compounds are much less reactive than alkenes. The reason for this decrease in reactivity is the large amount of stabilization present in aromatic compounds as a result of their special cycle of conjugated *p* orbitals. This great difference in reactivity is the reason why aromatic compounds are classified separately from the alkenes. As an example of this reactivity difference, the treatment of benzene with $Cl_2$ under conditions in which the $Cl_2$ would rapidly add to an alkene does not result in any reaction. Under more drastic conditions, in the presence of a Lewis acid catalyst such as $AlCl_3$, a reaction does occur, but the product retains the conjugated system of the aromatic ring. Rather than the addition reaction that would have resulted with an alkene, a chlorine replaces one of the hydrogens on the ring. This reaction, in which one group replaces an-

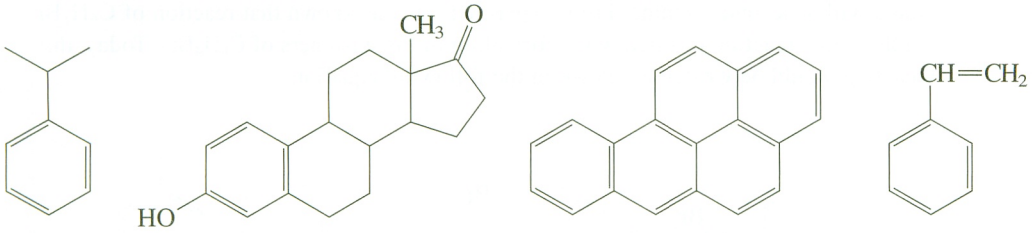
other, is another type of substitution reaction and is the most important reaction of aromatic compounds.

**Substitution Reaction:**




Benzene Chlorobenzene

Because of their stability, aromatic compounds are found in a variety of natural sources. Often the aromatic ring occurs in combinations with other functional groups. Benzene itself was first isolated, by Michael Faraday in 1825, from the oily residue that condensed from the gas that was used to light the street lamps of London. A few examples of other naturally occurring compounds that contain aromatic rings are cumene (isopropylbenzene), which occurs in petroleum; estrone, a female sex hormone that has an aromatic ring as part of a complex ring system; and benzo[a]pyrene, which consists of a series of fused aromatic rings. Benzo[a]pyrene is a carcinogenic (cancer-causing) substance produced upon combustion of many materials. It is found in soot and is one of the major carcinogens found in tobacco smoke.




Cumene Estrone Benzo[a]pyrene Styrene

Benzene is one of the major chemicals produced by the petroleum industry. More than 1.6 billion gallons are produced each year by cracking and reforming various petroleum fractions. Most of this is used in the production of styrene, which is then polymerized to polystyrene. Other arenes that are made in large amounts include toluene (830 million gallons), cumene, *o*-xylene, and *p*-xylene. At one time, benzene was an important solvent in the organic laboratory. Recently, however, its use has been phased out because of its potential adverse health effects. Long exposure to benzene has been shown to lead to bone marrow depression and leukemia.

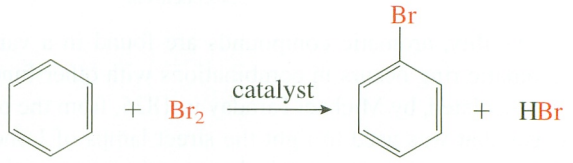
# Focus On

## Structure Proof by the Number of Isomers

How did organic chemists identify the structures of organic compounds before the advent of spectroscopy? Basically, the structure had to be consistent with all the facts known about a compound. Often, these facts included the results of a number of chemical reactions. Let's examine the case of the substitution products that occur on reaction of benzene with bromine.

*Continued*

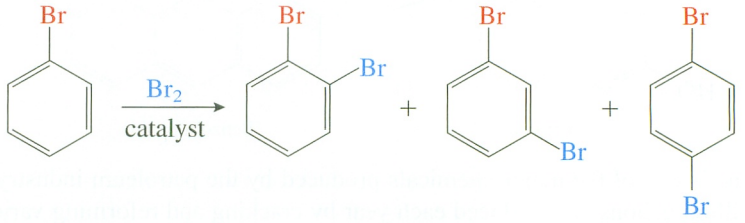
In 1866, August Kekulé, one of the true pioneers of organic chemistry, proposed a structure for benzene that is remarkably similar to the structure used today. From experiments, he knew that substitution reactions of benzene always gave a single monosubstitution product. For example, the reaction of benzene ($C_6H_6$) with bromine in the presence of aluminum tribromide as a catalyst gave only one monobromide ($C_6H_5Br$). This indicates that all of the hydrogens of benzene must be identical. One of the structures that satisfies the valence rules and this observation is a six-membered ring with three double bonds:




Benzene Bromobenzene

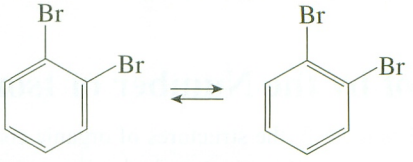
In this structure for benzene, all the carbons are identical, so it does not matter which one bonds to the bromine in the substitution reaction; only one monobromo substitution product is possible.

Kekulé next considered what would happen if bromobenzene were further substituted with a second bromine. From experiment, it was known that reaction of $C_6H_5Br$ in this same reaction resulted in the formation of three isomers of $C_6H_4Br_2$. Today, this reaction would be written as shown in the following equation:




ortho meta para

However, to make the results of this reaction consistent with his theory, Kekulé had to make some modifications. To see the problem, it is necessary only to recall that the concept of resonance had not yet been proposed at this point in the development of organic chemistry. Kekulé realized that, according to his structural theory, there should be two products related to the ortho product, one with a single bond between the carbons attached to the bromines and one with a double bond between these carbons.



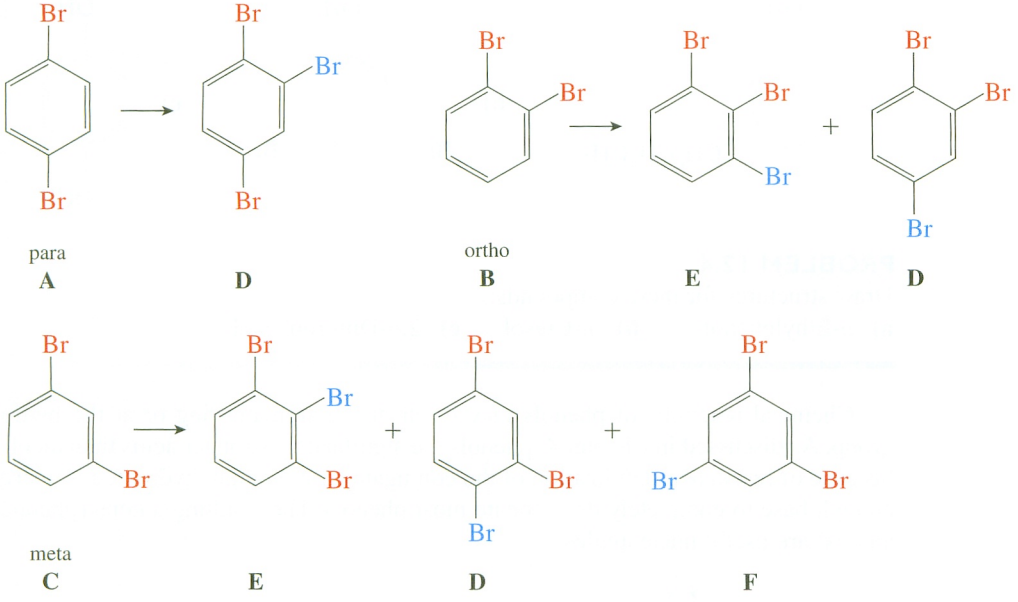

To make his theoretical prediction (four products) consistent with experimental observation (three products), Kekulé proposed that the two "*ortho*-isomers" were actually in rapid equilibrium and therefore behaved as a single compound. Of course,

today we know that these are two resonance structures of *ortho*-dibromobenzene rather than distinct isomers, but Kekulé's proposal was not too far removed from our current ideas.

Now let's carry our considerations one step further. As we know, bromination of bromobenzene produces three isomers of dibromobenzene. One of these is the *ortho*-isomer, one is the *meta*, and one is the *para*, but which is which? This question was answered by Wilhelm Korner in 1874, who reacted each of the $C_6H_4Br_2$ isomers under substitution conditions that produced the tribrominated products, $C_6H_3Br_3$. By determining the number of isomeric tribromides produced from each dibromide, he was able to assign the structures of all of the compounds. He found that one $C_6H_4Br_2$ isomer, call it **A,** produced a single isomer of $C_6H_3Br_3$, call it **D.** Another isomer of $C_6H_4Br_2$, **B,** produced two isomers of $C_6H_3Br_3$: **D** (obtained previously) and a new isomer, **E.** The final isomer of $C_6H_4Br_2$, **C,** produced three isomers of $C_6H_3Br_3$: **D, E,** and a new isomer, **F.** These results are summarized in the following equations:

| Dibromide | | Tribromide | |
|---|---|---|---|
| **A** | ⟶ | **D** | (one product) |
| **B** | ⟶ | **D + E** | (two products) |
| **C** | ⟶ | **D + E + F** | (three products) |

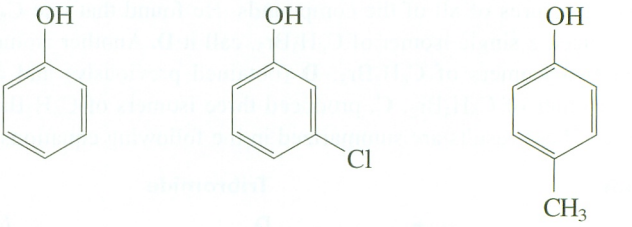
The products predicted to result from the bromination of the *ortho*-, *meta*-, and *para*-isomers of dibromo benzene are as follows:


Br
Br
Br

## 12.2 PHENOLS

**Phenols** are compounds that have a hydroxy group bonded directly to an aromatic ring. The delocalization of the electrons on the oxygen onto the aromatic ring changes the reactivity of the hydroxy group enough that phenols are given their own functional group rather than being classified with alcohols.

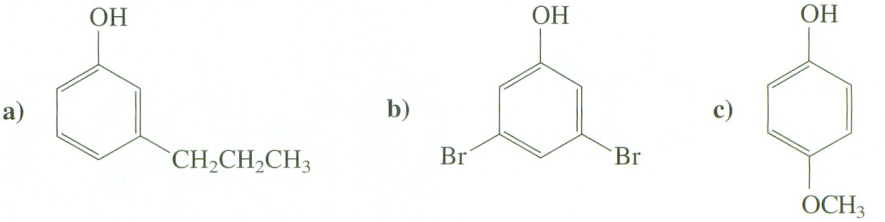
The simplest member of this class of compounds is named phenol. Others can be named as substituted phenols, although numerous common names may be encountered.




Phenol | *m*-Chlorophenol | *p*-Methylphenol (*p*-cresol)

### PROBLEM 12.3

Provide names for these compounds:

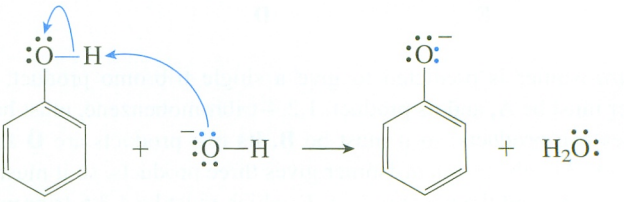



### PROBLEM 12.4

Draw structures for these compounds:

**a)** *o*-Ethylphenol **b)** *m*-Cresol **c)** 2,6-Dinitrophenol

Chemical reactions of phenols may occur at the aromatic ring or at the hydroxy group. As discussed in Chapter 4, phenols are significantly stronger acids than alcohols because of resonance stabilization of the conjugate base. Sodium hydroxide is a strong enough base to completely deprotonate most phenols. The resulting anions (phenolate anions) are useful nucleophiles.



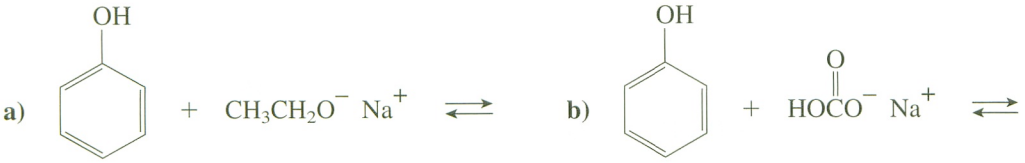

Phenol | Phenolate anion

**PROBLEM 12.5**

Show the resonance structures for the conjugate base of phenol.

**PROBLEM 12.6**

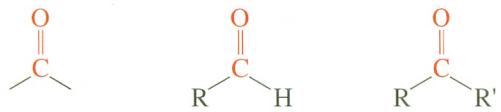
The p$K_a$ for phenol is 10, the p$K_a$ for ethanol is 16, and the p$K_a$ for carbonic acid ($H_2CO_3$) is 6.35. Complete these equations and predict whether the reactants or the products are favored at equilibrium.




Phenol is an important industrial chemical. More than 3 billion pounds are produced each year. The major uses of phenol are as a disinfectant and in the production of polymers. Complex phenols, with multiple substituents and functional groups, are common in nature, although the simple phenols are seldom encountered.

## 12.3 ALDEHYDES AND KETONES

A carbon–oxygen double bond is called a **carbonyl group.** Compounds that contain a carbonyl group are among the most important in organic chemistry because of the varied reactions that they undergo. **Aldehydes** have at least one hydrogen atom bonded to the carbonyl group (the other atom can be hydrogen or carbon). In the case of **ketones,** both of the atoms bonded to the carbonyl group must be carbons.



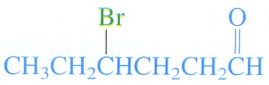

Carbonyl group | Aldehyde | Ketone

As with the other functional groups encountered so far, the first step in naming an aldehyde is finding the longest chain that contains the functional group—the carbonyl group in this case. Because the carbonyl group of an aldehyde must be at the end of the chain, numbering *always* begins with the carbonyl carbon. The suffix used to designate an aldehyde is -al.

Common names for simple aldehydes are frequently encountered. These common names are derived from the common names for the related carboxylic acid (see Section 12.4) by replacing the suffix -ic acid with the suffix -aldehyde. Thus, the aldehyde related to acetic acid is acetaldehyde. If the carbonyl group of an aldehyde is attached to a ring system, the compound can be named as a hydrocarbon with the suffix -carbaldehyde. (Some sources use -carboxaldehyde.)

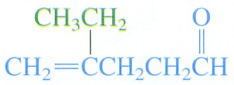
Ethanal

(The common name is acetaldehyde, derived from acetic acid.)



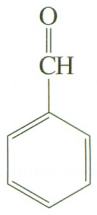
4-Bromohexanal

(No number is needed to designate the position of the carbonyl carbon of an aldehyde because it is always located at position 1.)



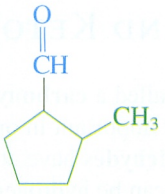
4-Ethyl-4-pentenal

(The longest chain containing the carbonyl carbon *and* the carbon–carbon double bond is chosen as the root. Again, numbering begins with the carbonyl carbon.)



Benzaldehyde

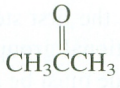
(This name, derived from benzoic acid, is also the systematic name for this aldehyde. It is used to name substituted derivatives.)



2-Methylcyclopentanecarbaldehyde

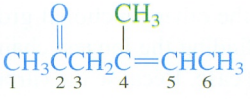
(The suffix -carbaldehyde indicates that the —CHO group is attached to the parent ring.)

To name ketones, the longest chain containing the carbonyl carbon is again chosen as the parent. This chain is numbered so that the carbonyl carbon has the lowest possible number, and the suffix -one is used. Common names are also encountered occasionally.



2-Propanone

(This compound is usually called by its common name, acetone.)

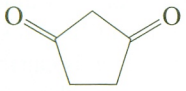


4-Methyl-4-hexen-2-one

or

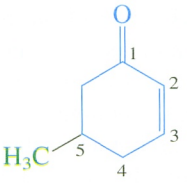
4-methylhex-4-en-2-one

(Choose the parent so that it includes both the carbonyl group and the carbon–carbon double bond. Number so that the carbonyl carbon gets the lower number.)



1,3-Cyclopentanedione
or
cyclopentane-1,3-dione

(Note the "e" that is added between "cyclopentan" and "dione" to aid in pronunciation.)



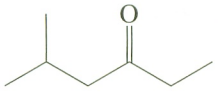
5-Methyl-2-cyclohexenone
or
5-methylcyclohex-2-enone

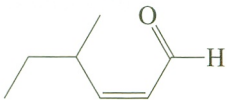
(Number so that first the carbonyl group and then the carbon–carbon double bond get the lowest possible numbers.)

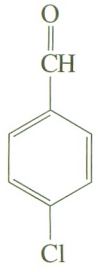
**PROBLEM 12.7**

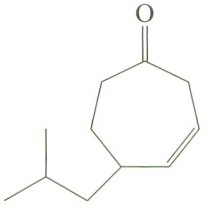
Provide names for these compounds:

**a)** $CH_3CH_2CH_2CH_2CH_2\overset{\overset{O}{\|}}{C}H$

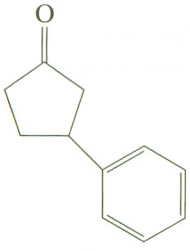
**b)** 

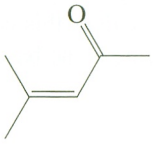
**c)** 

**d)** 

**e)** 

**f)** $CH_3\overset{\overset{O}{\|}}{C}CH_2\overset{\overset{O}{\|}}{C}CH_3$

**g)** 

**h)** 

**PROBLEM 12.8**

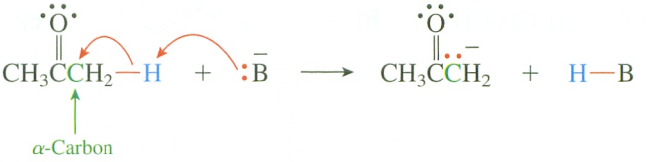
Draw structures for these compounds:

**a)** (*Z*)-Oct-3-en-2-one
**b)** 3-Ethylheptanal
**c)** 2,4-Pentadienal
**d)** 3,4-Dimethylbenzaldehyde
**e)** 1-Phenyl-1-propanone
**f)** 2,2,6,6-Tetramethylcyclohexanone

ORGANIC Chemistry Now™
Click *Coached Tutorial Problems* for more practice **Drawing Structures of Aldehydes and Ketones from IUPAC Names.**

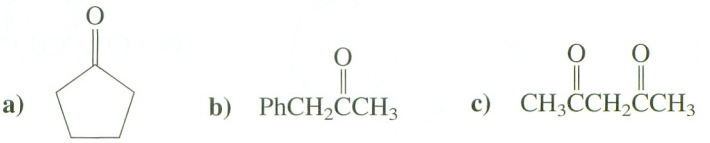
The carbonyl group of an aldehyde is more polar than a carbon–oxygen single bond. However, a molecule of an aldehyde does not have a hydrogen on an electronegative atom, so it is incapable of forming a hydrogen bond with other aldehyde molecules. Therefore, the boiling point of an aldehyde is higher than that of a similar ether, which is less polar, but lower than that of a similar alcohol, which is capable of hydrogen bonding with other alcohol molecules. Because the oxygen of the carbonyl group can act as the Lewis base partner in a hydrogen bond, lower molecular weight aldehydes are, like alcohols, relatively water soluble. Similar arguments apply to ketones.

Aldehydes and ketones share many chemical reactions because both have a carbonyl group. Often their reactions begin with an acid–base step. As discussed in Chapter 4, the protons on the carbon adjacent to a carbonyl group, called the ***α*-carbon,** are weakly acidic, with a $pK_a$ of about 20. A strong base can remove a proton from the α-carbon, as illustrated in the following equation. One feature that distinguishes aldehydes from ketones is the fact that aldehydes can be oxidized to carboxylic acids (see Section 10.14), whereas ketones are inert to most oxidizing agents. Aldehydes and ketones are among the most useful functional groups in the organic laboratory because of the wide variety of reactions that they undergo.



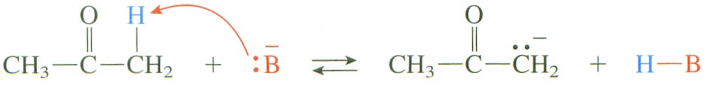

## PROBLEM 12.9

Explain which are the most acidic hydrogens in these compounds:



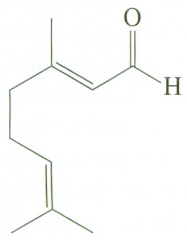

## PROBLEM 12.10

**a)** Is sodium hydroxide a strong enough base to completely remove a proton from the α-carbon of acetone; that is, does this equilibrium lie nearly completely to the right when sodium hydroxide is the base?

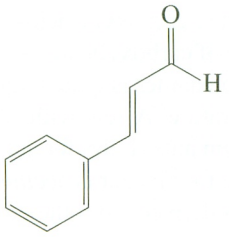


**b)** Which common bases can be used to completely remove a proton from acetone? (See Table 4.4 on page 131.)

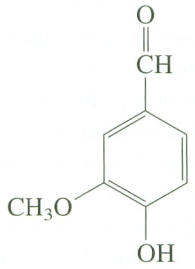
Aldehydes and ketones often have pleasant odors. They are found as components of many perfumes and flavorings, both natural and artificial. For example, citral has a strong lemon odor and is found in lemon and orange oils, cinnamaldehyde has a strong cinnamon odor and is found in cinnamon oil, and vanillin is a major component of vanilla flavoring. Camphor, isolated from the camphor tree, is used in liniments and inhalants, and muscone, which has a "musky" aroma, is used in many perfumes.



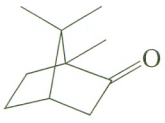
Citral



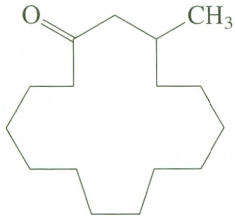
Cinnamaldehyde



Vanillin



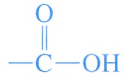
Camphor



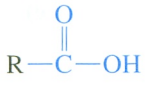
Muscone
(3-methylcyclopentadecanone)

## 12.4 CARBOXYLIC ACIDS

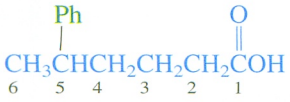
**Carboxylic acids** are compounds containing a carboxy group, that is, a carbonyl group with an attached hydroxy group. The systematic name for a carboxylic acid uses as the root the longest chain with the carboxy group at one end with the suffix -oic acid added. As with aldehydes, the chain is always numbered beginning with the carbon of the carboxy group.



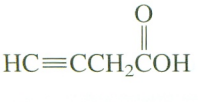
Carboxy group



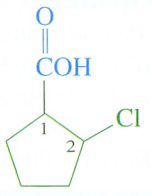
Carboxylic acid



5-Phenylhexanoic acid
(Numbering always begins with the carboxy carbon.)

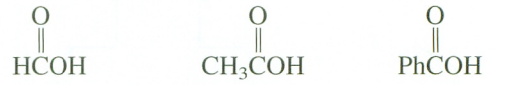


3-Butynoic acid



2-Chlorocyclopentanecarboxylic acid
(In similar fashion to the use of the -carbaldehyde suffix in naming aldehydes, cyclic compounds with the carboxy group attached to the ring use the name of the ring with the suffix -carboxylic acid.)

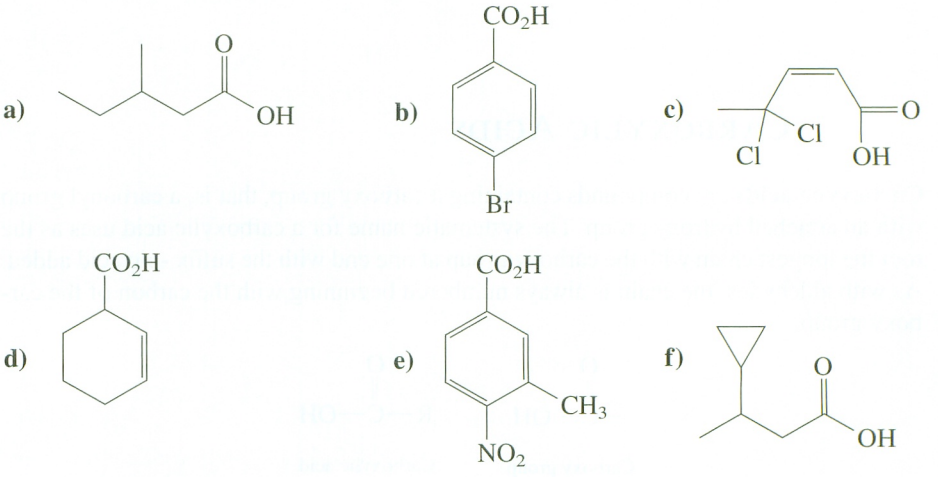
Because of their acidic character, carboxylic acids are relatively easy to isolate from natural sources. Thus, the number of carboxylic acids isolated early in the history of organic chemistry and given common names is quite large. Many of these common names have persisted in the organic literature. A few with which you should be familiar are formic acid, originally isolated from ants (Latin for ant is *formica*) and acetic acid, originally isolated from vinegar (Latin for vinegar is *acetum*). As mentioned earlier, the root for a four-carbon chain, but-, was derived from the common name for the four-carbon acid, butyric acid, which was isolated from rancid butter (Latin for butter is *butyrum*). Similarly, the root for a three-carbon chain, prop-, was derived from the common name for the three-carbon acid, propionic acid. This acid was considered to be the smallest one derived from fats and its name is derived from the Greek words *pro-* (first) and *pion* (fat). Aromatic carboxylic acids are named as derivatives of benzoic acid.




Formic acid (methanoic acid) | Acetic acid (ethanoic acid) | Benzoic acid

**PROBLEM 12.11**

Provide names for these compounds:




**PROBLEM 12.12**

Draw structures for these compounds:

**a)** 6-Bromo-3,5-dichlorohexanoic acid
**b)** Cyclobutanecarboxylic acid
**c)** *m*-Chlorobenzoic acid
**d)** (*E*)-3-Phenyl-2-propenoic acid

The carboxy group is more polar than a carbonyl group or a hydroxy group, and it can form hydrogen bonds to other carboxy groups. Therefore, carboxylic acids melt and boil at somewhat higher temperatures than alcohols of similar molecular weight. As was

the case with alcohols, the smaller carboxylic acids are miscible with water. As expected, their solubility decreases as the size of the hydrocarbon group increases.

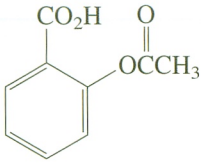
**PROBLEM 12.13**

Hydrogen bonding is quite strong in the case of acetic acid and persists even in the gas phase where two molecules form a dimer held together by two hydrogen bonds. Suggest a structure for the hydrogen-bonded dimer of acetic acid.

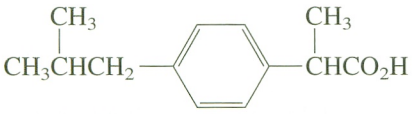
Carboxylic acids are weak acids ($pK_a \approx 5$) and react by donating the proton attached to the oxygen of the carboxy group as illustrated in the following equation:

Acetic acid

Although carboxylic acids do occur naturally, they most often are found as their ester or amide derivatives. Acetic acid is a major industrial chemical, produced in excess of 3 billion pounds annually. Some acids, such as acetylsalicylic acid (aspirin) and ibuprofen, have found considerable use in the medical field.



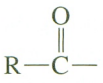
Acetylsalicylic acid (aspirin)



Ibuprofen

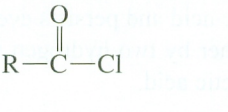
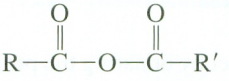
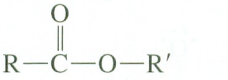
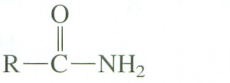
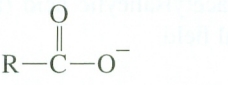
## 12.5 Derivatives of Carboxylic Acids

Removal of the hydroxy group of a carboxylic acid leaves a carbonyl group with an attached alkyl group, which is called an **acyl group.** If the acyl group is bonded to a hydrogen, an aldehyde results. If it is bonded to a carbon, a ketone results. And if it is bonded to a hydroxy group, a carboxylic acid is produced. However, if the acyl group is bonded to another **heteroatom** (not C or H) group, such as Cl or $NH_2$, a series of compounds called carboxylic acid derivatives is produced. The most important of these, along with their names and the suffixes used in their nomenclature, are listed in Table 12.1.



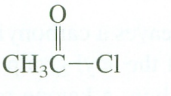
Acyl group

**Table 12.1 Carboxylic Acid Derivatives**

| Structure | Name of Functional Group | Suffix |
|---|---|---|
|  | Acid chloride or acyl chloride | -yl chloride |
|  | Acid anhydride | -ic anhydride |
|  | Ester | -ate |
|  | Amide | -amide |
| | Nitrile | -nitrile |
|  | Carboxylate salt | -ate |

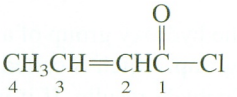
Carboxylic acid derivatives are all named by using the same root as the carboxylic acid from which they are derived. Note that the root always begins with the carbon of the carbonyl group and this carbon is always given the number 1.

**Acid chlorides** (or **acyl chlorides**) result from substituting a chlorine for the hydroxy group of a carboxylic acid. Although other acid halides also exist, they are seldom encountered. Acid chlorides are named by replacing the -ic acid of the carboxylic acid name (either common or systematic) with -yl chloride.



Acetyl chloride
(ethanoyl chloride)

(The common and most used name for the related carboxylic acid is acetic acid. The -ic acid is replaced by -yl chloride.)

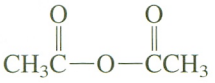


2-Butenoyl chloride

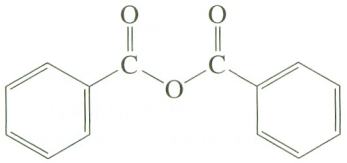
(The corresponding carboxylic acid is 2-butenoic acid.)

**Acid anhydrides** result from substituting the acyl group of one acid for the hydroxy hydrogen of another. They are called anhydrides because they can be viewed as resulting from the loss of water from two carboxylic acid molecules (removing H from one and OH from the other). Symmetrical anhydrides derived from two molecules of the

same carboxylic acid are most often encountered. These are simply named by replacing *acid* in the name of the carboxylic acid with *anhydride*.

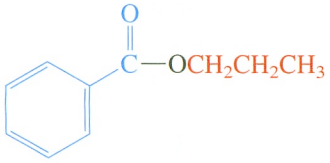


Acetic anhydride
(ethanoic anhydride)

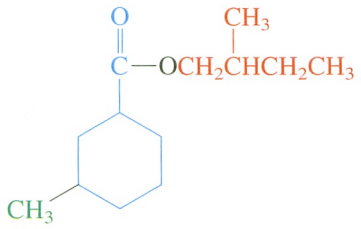


Benzoic anhydride

**Esters** can be viewed as resulting from the combination of a carboxylic acid with an alcohol, using the alkoxy (OR) group of the alcohol to replace the hydroxy (OH) group of the acid. The name must therefore designate both the alcohol part and the acid part of the ester. The name uses two separate words. First the R group of the alcohol is named just like other *groups* we have encountered, using a -yl suffix. This is the first word in the name. Then the acid part is named as usual, and the -ic acid suffix is replaced with -ate. This is the second word in the name.

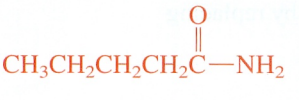


Propyl benzoate
(The red part of this ester is derived from the alcohol [propanol], and the blue part from the carboxylic acid [benzoic acid]. Be careful to correctly identify which part of each ester comes from the acid and which from the alcohol. Note that *propyl* and *benzoate* are separate words.)

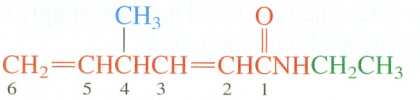


(2-Methylbutyl) 3-methylcyclohexanecarboxylate
(The complex group from the alcohol portion of the ester is named in the same manner as the complex groups of alkanes.)

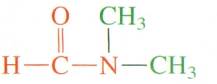
**Amides** can be viewed as resulting from the replacement of the OH of a carboxylic acid with an $NH_2$ (primary amide), NHR (secondary amide), or $NR_2$ (tertiary amide) group. To name an amide, the longest carbon chain having the carbonyl group at one terminus is chosen as the root, as usual. Systematic names are formed by replacing the final -e of the *hydrocarbon name* for this root with -amide. Amide names can also be derived from common names of acids by replacing -ic acid or -oic acid with -amide. Other groups attached to the nitrogen are designated with the prefix *N*-, as was done in the case of amines.



Pentanamide
a primary amide
(This name is derived from the five carbon hydrocarbon, pentane.)



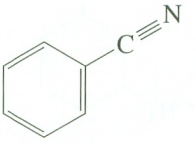
*N*-Ethyl-4-methyl-2,5-hexadienamide
or *N*-ethyl-4-methylhexa-2,5-dienamide
a secondary amide
(Note the *N*- that is used to show that the ethyl group is bonded to the nitrogen.)



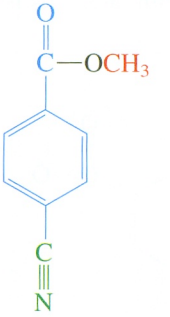
*N,N*-Dimethylformamide
(DMF), a tertiary amide
(The common name for the one-carbon carboxylic acid is formic acid.)

On first consideration, **nitriles** do not appear to be related to the other carboxylic acid derivatives because they have no acyl group. However, they can be viewed as resulting from the removal of $H_2O$ from a primary amide (loss of both H's from the N and the O from the carbonyl group), and their chemical reactions are related to other carboxylic acid derivatives. Therefore, it is convenient to include them with the other carboxylic acid derivatives. They are named in a similar manner to amides; that is, -nitrile is appended to the hydrocarbon name. (Do not forget to count the carbon of the —CN group and to give this carbon the number 1.) Common names are obtained from the common name of the carboxylic acid by replacing the -ic acid or -oic acid with -onitrile. In complex compounds the —CN group can be named as a cyano group.

3-Pentynenitrile
(This is a systematic name. Because the C of the CN must be given the number 1, the related hydrocarbon is 3-pentyne.)

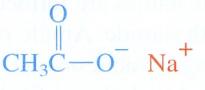


Benzonitrile
(The related carboxylic acid is benzoic acid.)

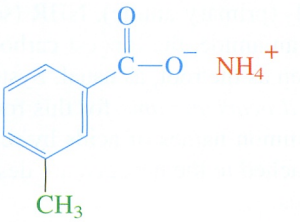


Methyl 4-cyanobenzoate
(In a complex compound like this, with more than one functional group, the —CN is named as a substituent group, a cyano group, attached to the root in the same manner as a halogen.)

**Carboxylate salts** consist of a carboxylate anion (the anion formed by removal of the proton from the OH of a carboxylic acid) and a cation. They are named in a manner similar to esters, using two words. The first word designates the cation. The second word designates the carboxylate anion, using the -ate suffix, just as is done for esters.



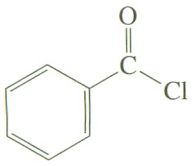
Sodium acetate



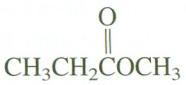
Ammonium 3-methylbenzoate

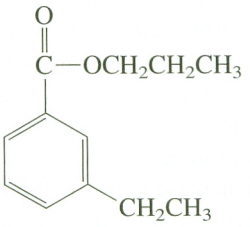
**PROBLEM 12.14**

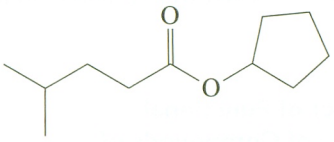
Provide names for these compounds:

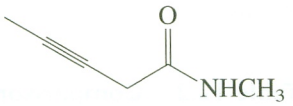
**a)** 

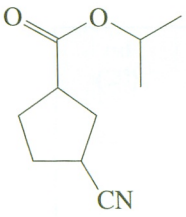
**b)**

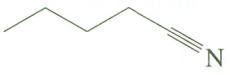
**c)** 

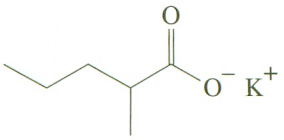
**d)** 

**e)** 

**f)** 

**g)** 

**h)** 

**i)** 

**PROBLEM 12.15**

Draw structures for these compounds:

**a)** Propanoyl chloride
**b)** *N*,*N*-Dimethylacetamide
**c)** Pentanoic anhydride
**d)** Sodium *p*-nitrobenzoate
**e)** Hexanamide
**f)** Isopropyl acetate
**g)** Benzyl benzoate
**h)** Ethyl cyclopentanecarboxylate
**i)** 3-Chlorobenzonitrile
**j)** 3-Methylheptanenitrile

ORGANIC Chemistry Now™
Click *Coached Tutorial Problems* for more practice **Drawing Structures of Carboxylic Acids and Derivatives from IUPAC Names.**

Acid chlorides, acid anhydrides, and esters all contain the carbonyl group but the presence of this polar group has only a small effect on their melting and boiling points. Amides, however, are considerably more polar because of the significant contribution of a charged resonance structure to the resonance hybrid. In addition, primary and secondary amides, with hydrogens bonded to the nitrogen, can also form hydrogen bonds

among themselves. For these reasons, amides melt and boil at even higher temperatures than do carboxylic acids of similar molecular mass.

An amide

Table 12.2 lists the melting points and boiling points of a series of compounds of nearly identical molecular mass but containing a variety of different functional groups. Note the increase in the melting point and boiling point that occurs when the polar carbonyl group is introduced. The effect is small (or may be absent) for the ester but is more significant for the aldehyde and ketone, especially on their boiling points. There is an additional increase in the boiling point for the alcohol due to hydrogen bonding and a further increase in the melting and boiling points of the carboxylic acid due to its polar, hydrogen-bonding carboxy group. Finally, the amide has the highest melting and boiling points because of its highly polar nature in combination with its ability to form hydrogen bonds.

**Table 12.2 Comparison of the Effect of Functional Groups on Melting and Boiling Points of Compounds of Comparable Molecular Mass**

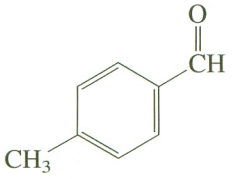
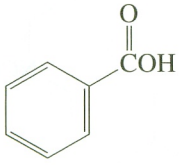
| Structure | Functional Group | mp (°C) | bp (°C) |
|---|---|---|---|
| $CH_3CH_2CH_2CH_2CH_3$ | Alkane | −130 | 36 |
| $CH_3CH_2OCH_2CH_3$ | Ether | −116 | 35 |
| $CH_3\overset{\overset{O}{\|}}{C}OCH_3$ | Ester | −98 | 57 |
| $CH_3CH_2CH_2\overset{\overset{O}{\|}}{C}H$ | Aldehyde | −99 | 76 |
| $CH_3CH_2\overset{\overset{O}{\|}}{C}CH_3$ | Ketone | −86 | 80 |
| $CH_3CH_2CH_2CH_2OH$ | Alcohol | −90 | 117 |
| $CH_3CH_2\overset{\overset{O}{\|}}{C}OH$ | Carboxylic acid | −21 | 141 |
| $CH_3CH_2\overset{\overset{O}{\|}}{C}NH_2$ | Amide | 81 | 213 |

**PROBLEM 12.16**

Explain which compound has the higher melting point or boiling point:

**a)** Higher mp $CH_3CH_2CH_2\overset{\overset{O}{\|}}{C}NH_2$ or $CH_3\overset{\overset{O}{\|}}{C}N(CH_3)_2$

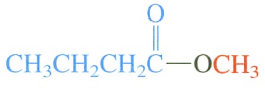
**b)** Higher bp $CH_3CH_2CH_2\overset{\overset{O}{\|}}{C}OH$ or $CH_3CH_2\overset{\overset{O}{\|}}{C}OCH_3$

**c)** Higher bp  or 

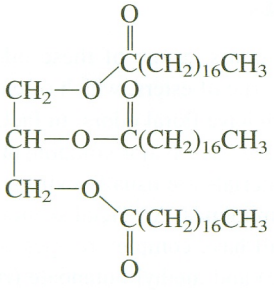
**d)** Higher mp $CH_3CH_2CH_2\overset{\overset{O}{\|}}{C}OH$ or $CH_3CH_2CH_2\overset{\overset{O}{\|}}{C}NH_2$

In general, acid chlorides and acid anhydrides are too reactive to occur naturally, and nitriles are rare in nature. Esters and amides, on the other hand, are very common. Many esters have pleasant odors, often sweet or fruity, and are responsible for the fragrant odors of fruits and flowers. They are components of many flavorings, both natural and artificial. For example, isopentyl acetate has a strong banana odor, and methyl butanoate is used as an artificial rum flavoring. Typical fats are triesters formed from long-chain "fatty" acids and the triol glycerol.

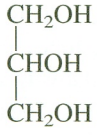
Isopentyl acetate



Methyl butanoate



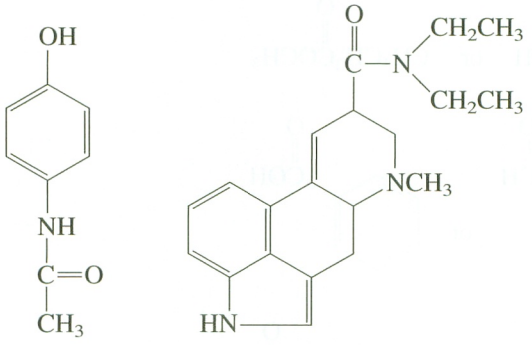
A fat



Glycerol

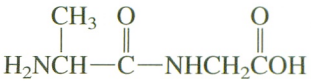
Amides often have pronounced physiological activity; acetaminophen, a common pain reliever, and the diethyl amide of lysergic acid (LSD), a hallucinogen, are two ex-

amples. The important peptide bond of proteins is actually an amide bond. Dimethylformamide (DMF) and dimethylacetamide (DMA) are important solvents in the organic laboratory. They are highly polar and are capable of dissolving many ionic reagents in addition to less polar organic compounds. They are fairly unreactive because the bond between the carbonyl group and the nitrogen of an amide is reasonably strong, and they do not have hydrogens on the nitrogens that might react as acids. They are especially good solvents for $S_N2$ reactions because they are aprotic.



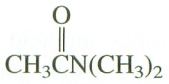

Acetaminophen

Lysergic acid diethylamide (LSD)




A dipeptide

Dimethylformamide (DMF)



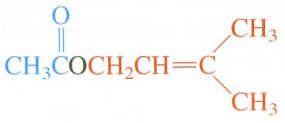

Dimethylacetamide (DMA)

# Focus On

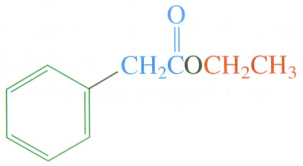
## Fragrant Organic Compounds

Many organic compounds have very powerful odors. Some of these odors are disagreeable; others are pleasant. This is especially true of esters, which often have fruity odors, and aldehydes and ketones, many of which have floral odors. In fact, aldehydes, ketones, and esters, with relatively simple structures, are major components of numerous natural scents and flavors. These natural materials are usually extremely complex mixtures, sometimes containing hundreds of compounds. Artificial scents and flavors usually contain fewer components, but many still have complex recipes consisting of dozens of ingredients. Isopentyl acetate (banana) and methyl butanoate (rum) are examples of fragrant esters that were mentioned earlier. Other examples include isopentenyl acetate, the flavoring used in Juicy Fruit gum; ethyl phenylacetate, which has a honey odor; methyl salicylate, a major component of oil of wintergreen; and benzyl acetate, which composes more than 60% of jasmine oil. Coumarin has an odor that is of-

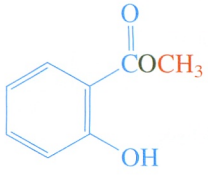
ten described as "new-mown hay" or "woody" and is used in men's toiletries. Along with vanillin (see page 477), it is a component of natural vanilla. A combination of these two compounds, prepared synthetically in the laboratory, is used in artificial vanilla, and the flavoring in cream soda consists of coumarin and vanillin.



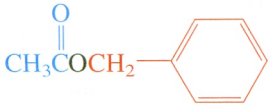
Isopentenyl acetate
(Juicy Fruit gum)



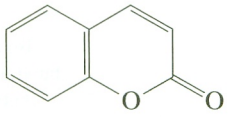
Ethyl phenylacetate
(honey)



Methyl salicylate
(wintergreen)



Benzyl acetate
(jasmine)

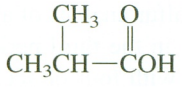


Coumarin
(new-mown hay)

Although many esters are used in artificial flavorings, they are less often employed as ingredients of perfumes because they are slowly hydrolyzed to a carboxylic acid and an alcohol on the skin, as shown in the following equation:

This is quite undesirable in a perfume because many carboxylic acids have objectionable odors. For example, the sharp, penetrating odor of vinegar is due to acetic acid, butanoic acid (butyric acid) smells like rancid butter, and 2-methylpropanoic acid (isobutyric acid) is a component of sweat. A common name for hexanoic acid is caproic acid, derived from the Latin word *caper,* which means goat. If you have ever been around goats, perhaps you can imagine the odor of hexanoic acid.

Butanoic acid
(butyric acid)
(rancid butter)



2-Methylpropanoic acid
(isobutyric acid)
(sweat)

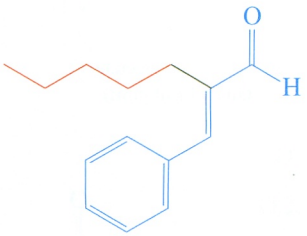
Hexanoic acid
(caproic acid)
(goat)

Aldehydes and ketones are also important components of many fragrances and flavors. For example, butanal (butyraldehyde) is used to impart a buttery flavor to margarine and other foods. Because aldehydes are slowly oxidized to carboxylic acids by the oxygen of air, it is readily apparent how the odor of rancid butter arises. Although $\alpha$-pentylcinnamaldehyde does not occur naturally, it has been found to have a powerful jasmine odor and is used in many perfumes and soaps. $\alpha$-Ionone is a naturally oc-

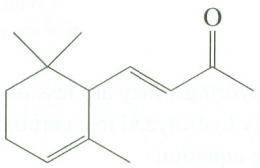
*Continued*

curring ketone with an odor resembling violets. Many large-ring ketones have a musky odor and are prized ingredients in perfumes. Muscone (see page 477), which was first isolated from the musk deer, has a 15-membered ring, and civetone, from the civet cat, has a 17-membered ring. These compounds were extremely expensive when they could only be obtained from natural sources. Once their structures were determined, they were prepared in the laboratory. Although the preparation of such large rings is difficult, these synthetic materials are still considerably less expensive than their natural counterparts. Other fragrant aldehydes and ketones are mentioned on pages 476–477.

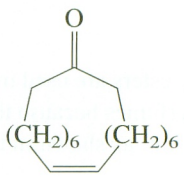
Butanal
butyraldehyde
(buttery)




α-Pentylcinnamaldehyde
(jasmine)




α-Ionone
(violets)



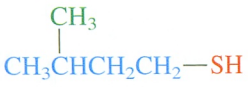

Civetone
(musky)

## 12.6 Sulfur and Phosphorus Compounds

Sulfur occurs directly beneath oxygen in the periodic table, and, like oxygen, it often exhibits a valence of two. Therefore, sulfur analogs of alcohols and ethers are often encountered. However, because sulfur is in the third period of the periodic table, it can also have a higher valence. Structures with four or six bonds to a sulfur are common. In organic chemistry the most important of these "expanded valence" compounds have the sulfur bonded to one or two extra oxygens.

Similarly, phosphorus occurs directly beneath nitrogen in the periodic table and therefore often exhibits a valence of three. Again, structures with an expanded valence, having five bonds to the phosphorus, are common, especially when the extra bonds are to oxygen. This book is not concerned with all the possible sulfur and phosphorus compounds, nor does it spend much time on their nomenclature. Instead, it concentrates on those of most importance in organic chemistry and biochemistry. Let's begin with a discussion of some common sulfur compounds.

Sulfur analogs of alcohols are called **thiols** or **mercaptans.** They are named in the same general manner as alcohols but with the suffix -thiol added to the name of the hydrocarbon. (In chemistry, thi- or thio-, from the Greek word for sulfur, *theion,* is used to indicate a compound that contains sulfur.) Thus, the sulfur analog of ethanol, $CH_3CH_2SH$, is named ethanethiol. Note that the "e" at the end of the hydrocarbon name is retained to aid in pronunciation. Sulfur analogs of ethers are called **sulfides.** They are named in the same general manner as ethers but with sulfide replacing ether in the name. Examples of thiols and sulfides include the following:



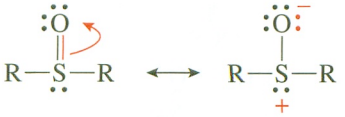
3-Methyl-1-butanethiol

2-Butene-1-thiol

Dimethyl sulfide

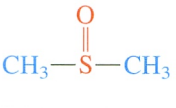
A characteristic of organic sulfur compounds, especially volatile (low molecular mass) thiols, is their disagreeable odors. For example, 3-methyl-1-butanethiol and 2-butene-1-thiol are ingredients of a skunk's "perfume," and methanethiol or ethanethiol is usually added, in small amounts, to natural gas, which is odorless by itself, so that leaks can be readily detected. The chemical properties of thiols and sulfides differ from those of alcohols and ethers in that thiols are somewhat stronger acids than alcohols and the sulfur atoms of these compounds are considerably more nucleophilic than the oxygen of their analogs. They are excellent nucleophiles in substitution reactions.

Other sulfur compounds of importance in organic chemistry have additional oxygens bonded to the sulfur, as in the **sulfoxide** and **sulfone** functional groups. (You may encounter sulfoxides written as either of their resonance structures.) The chemistry of these compounds is not covered in detail in this text. It is worth noting, however, that dimethylsulfoxide (DMSO) is an important solvent that is used in many organic reactions. It is quite polar, so it will dissolve both organic compounds and inorganic reagents, and it is fairly unreactive, so it will not interfere with many reactions. It is also aprotic.



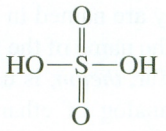
A sulfoxide

A sulfone

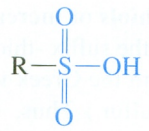


Dimethylsulfoxide (DMSO)

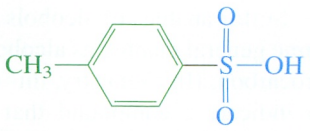
Another important group of sulfur-containing compounds can be viewed as being derived from sulfuric acid. Replacing one of the OH groups of sulfuric acid with a carbon group results in a new functional group called a **sulfonic acid.** Sulfonic acids are strong acids, comparable to sulfuric acid in strength. *p*-Toluenesulfonic acid is often used when a strong acid that is soluble in organic solvents is needed. The chemistry of sulfonic acids has some similarities to that of carboxylic acids. Thus, derivatives of sulfonic acid, like derivatives of carboxylic acids, include sulfonyl chlorides, sulfonate esters, and sulfonamides. As shown in the following examples, nomenclature of these compounds attaches -sulfon- to the hydrocarbon name and adds the same final suffixes as are used for the carboxylic acid derivatives.



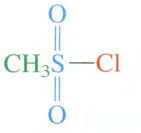
Sulfuric acid



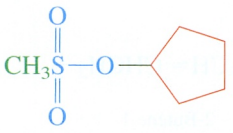
A sulfonic acid



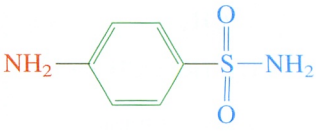
*p*-Toluenesulfonic acid
(The suffix -sulfonic acid is added to the hydrocarbon name.)



Methanesulfonyl chloride
(a sulfonyl chloride)

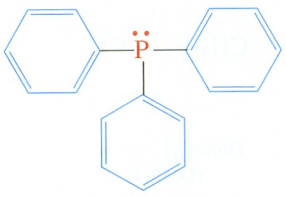


Cyclopentyl methanesulfonate
(a sulfonate ester)

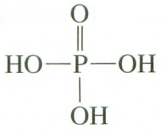


*p*-Aminobenzenesulfonamide
(a sulfonamide)
(This is better known as sulfanilamide, a sulfa drug.)

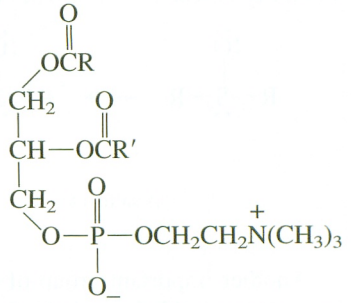
The phosphorus analogs of amines are called **phosphines.** The parent, $PH_3$, is called phosphine and is a toxic gas with an unpleasant odor. Triphenylphosphine is a good nucleophile that is employed in certain organic reactions. Esters derived from phosphoric acid play an important role in living organisms. One, two, or all three of the OH groups of phosphoric acid can be replaced with OR groups to form various phosphate esters. The anions produced by the ionization of dialkyl hydrogen phosphates in water by an acid–base reaction are especially important in biological systems. This group provides the backbone for DNA and RNA. As another example, phosphatidylcholine is a phospholipid that is an important constituent of cell membranes.



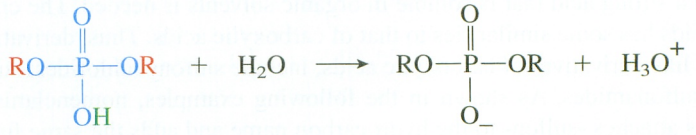
Triphenylphosphine



Phosphoric acid



Phosphatidylcholine

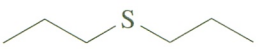


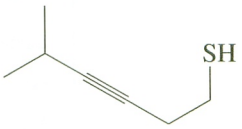
A dialkyl hydrogen phosphate

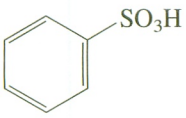
**PROBLEM 12.17**

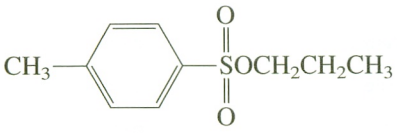
Provide names for these compounds:

a)


b) 


c) 


d) 


e) 

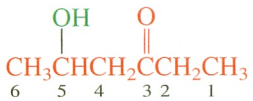

**PROBLEM 12.18**

Draw structures for these compounds:

**a)** 2-Butanethiol
**b)** Benzenethiol
**c)** Isopropyl methanesulfonate
**d)** *p*-Bromobenzenesulfonic acid
**e)** Phenyl trichloromethyl sulfide

## 12.7 Nomenclature of Compounds with Several Functional Groups

Most of the compounds that you have encountered in this text so far have been fairly simple. In addition to any carbon–carbon double or triple bonds, they have contained only one functional group and could be named by using suffixes such as -ynol or -dienone. However, for a compound that contains more than one heteroatom functional group, only one of these functional groups can be designated in the suffix. For example, consider the following compound, which has both alcohol and ketone functional groups:




5-Hydroxy-3-hexanone
or
5-hydroxyhexan-3-one

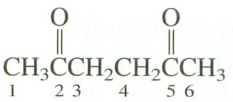
Because both functional groups cannot be denoted in the suffix, one must be chosen as higher priority and used to control both the numbering and the suffix. A prefix is then used to indicate the presence of the lower-priority functional group on the main chain. In the case of the preceding compound, the ketone group has a higher priority than the alcohol group, so an -one suffix is used. Numbering begins with the right carbon so that the carbon of the carbonyl group gets the lower number. The group name for OH is hydroxy. Therefore, the compound is named as 5-hydroxy-3-hexanone. Table 12.3 lists the

**Table 12.3 Order of Priority for Selected Functional Groups**

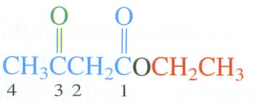
| Functional Group | Group Prefix | |
|---|---|---|
| Carboxylic acid | | Highest priority |
| Ester | | |
| Acid chloride | | |
| Amide | | |
| Aldehyde | oxo- | |
| Nitrile | cyano- | |
| Ketone | oxo- | |
| Alcohol | hydroxy- | |
| Amine | amino- | Lowest priority |
| Ether | alkoxy- | |
| Halogen | fluoro-, chloro- | |
| | bromo-, iodo- | |
| $-NO_2$ | nitro- | |

Note that the ether, halogen, and $-NO_2$ groups are always denoted by prefixes in systematic nomenclature.

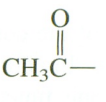
priorities and group names for selected other functional groups. Some examples of naming other complex molecules follow:



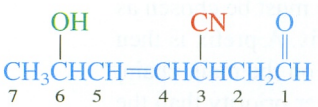
2,5-Hexanedione
or
hexan-2,5-dione
(The presence of several identical functional groups can be denoted with di-, tri-, etc.)



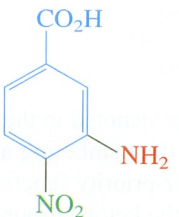
Ethyl 3-oxobutanoate
(ethyl acetoacetate)
(The ester group has higher priority, so it determines the numbering and the suffix. The ketone group is designated by the prefix oxo-. In common nomenclature the $CH_3C{=}O$ group is called acetyl or aceto.)



The acetyl or aceto group



3-Cyano-6-hydroxy-4-heptenal
(The aldehyde is the highest-priority functional group, so the OH and the CN must be denoted by their group prefixes.)



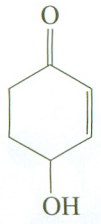
3-Amino-4-nitrobenzoic acid
(The acid group has the highest priority.)

**PROBLEM 12.19**

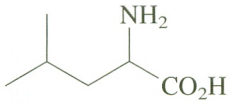
Provide systematic names for these compounds:

BioLink

**a)**



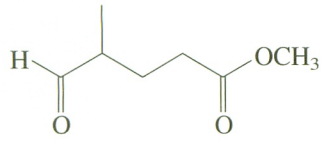
**b)**



Leucine
(an amino acid)

**c)**

**d)**



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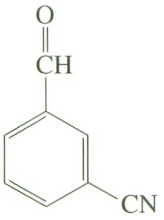

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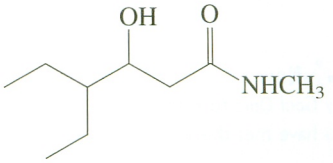

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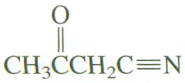

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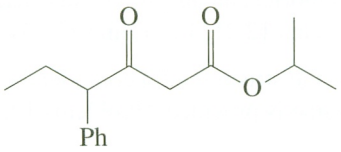


**PROBLEM 12.20**

Draw structures for these compounds:

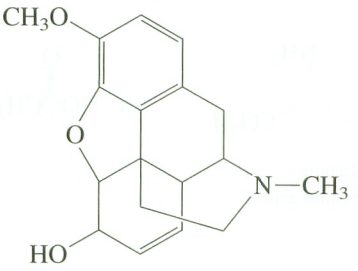
**a)** 1,6-Hexanedioic acid
**b)** Ethyl 2-ethyl-2-hydroxybutanoate
**c)** 2-Amino-3-cyclohexyl-1-propanol
**d)** *tert*-Butyl 2-hydroxy-5-octenoate
**e)** *N*,*N*,3-Trimethyl-2-oxobutanamide
**f)** 2-Amino-3-phenylpropanoic acid (an amino acid commonly called phenylalanine)

BioLink

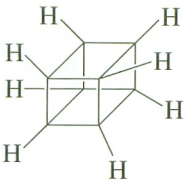
As you can see, organic nomenclature is a complex subject. Many of the rules and examples are beyond the scope of this book. You should not expect to be able to name every compound that you might encounter. However, based on the rules and examples given here and in Chapter 5, your knowledge of nomenclature should be sufficient to allow you to read and discuss organic chemistry.

Finally, you should realize that organic nomenclature is not an exact science. In complicated molecules there will often be ambiguities, and more than one correct systematic name may result. In addition, many complex molecules are best identified by a short common name rather than by a purely systematic name that is unmanageably long or complicated. As an example, the systematic name for codeine would be so complex that it would convey little immediate information about the compound to most chemists. In practice, therefore, common names continued to be coined for many molecules. For example, the systematic name pentacyclo[4.2.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]octane must be carefully analyzed by the average organic chemist, probably using pencil and paper, before its structure can be recognized. However, the common name given to this com-

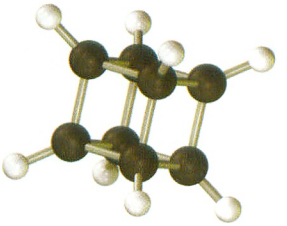
pound when it was first synthesized is very descriptive and immediately summons a mental picture for the compound. It is best known as cubane!




Codeine




Cubane



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## Review of Mastery Goals

***After completing this chapter, you should be able to:***

- Name an aromatic compound, a phenol, an aldehyde, a ketone, a carboxylic acid, an acid chloride, an anhydride, an ester, an amide, a nitrile, and a carboxylic acid salt. (Problems 12.21, 12.31, and 12.33)
- Draw the structure of a compound containing one of these functional groups when the name is provided. (Problems 12.22 and 12.32)
- Recognize the common functional groups that contain sulfur or phosphorus. (Problem 12.25)
- Name a compound containing more than one functional group or draw the structure of such a compound when the name is provided. (Problem 12.23)
- Understand how the physical properties of these compounds depend on the functional group that is present. (Problems 12.24, 12.34, 12.35, and 12.36)

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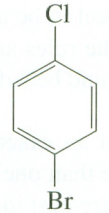
## Additional Problems

**12.21** Provide names for these compounds:

**a)**

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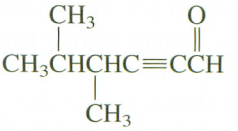


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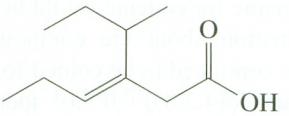


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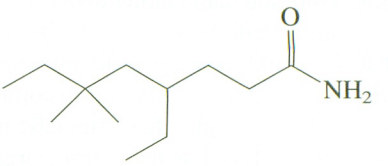
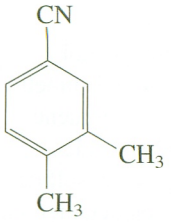


e) 

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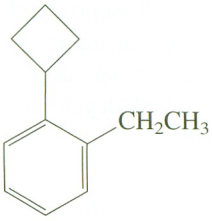
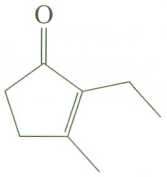
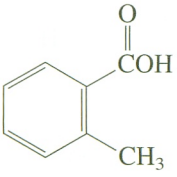
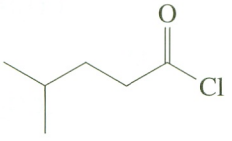
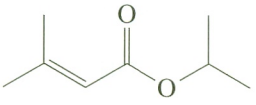
g) 

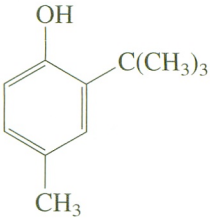
h) 

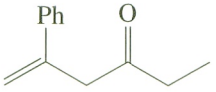
i) 

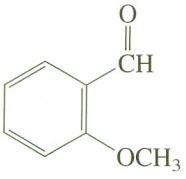
j) 

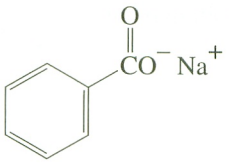
k)

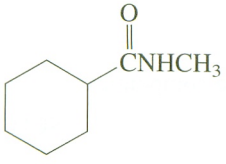
l) 

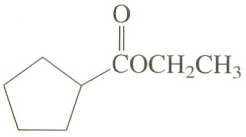
m) 

n) 

o) 

p) 

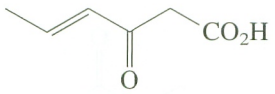
q) 

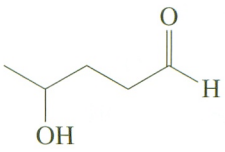
r) 

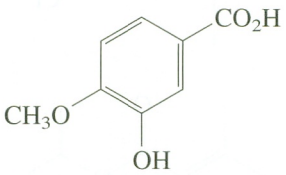
**12.22** Draw structures for these compounds:

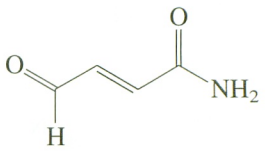
**a)** 3-Methoxybenzoic acid
**b)** *p*-Phenylphenol
**c)** 2-Methylbutyl *p*-toluenesulfonate
**d)** 4-Cyano-3,5-dimethyloctanal
**e)** Sodium acetate
**f)** 2,4-Dinitrotoluene
**g)** Ethyl 3-hydroxy-4-oxohexanoate
**h)** Acetyl chloride
**i)** Ethyl 2-chlorobenzoate
**j)** Phenyl vinyl sulfide
**k)** 1,2,4,5-Tetramethylbenzene
**l)** 2,4-Cyclooctadienone
**m)** Acetonitrile
**n)** Propyl 3-isopropyl-4-heptenoate
**o)** *N*-Methylpentanamide
**p)** 2,5-Hexanedione
**q)** 4-(1-Methylpropyl)benzaldehyde
**r)** Butanoic anhydride
**s)** 4-Hydroxyheptanoic acid
**t)** 2,2-Diethylcyclobutanecarboxylic acid

**12.23** Provide names for these compounds:

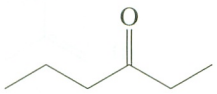
**a)** 

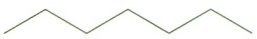

**b)** 

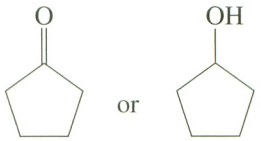

**c)** 

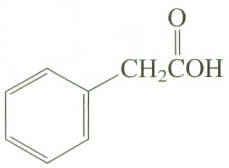

**d)** 

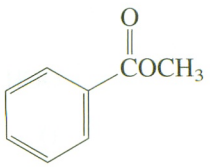

**12.24** Explain which compound has the higher melting point or boiling point:

**a)** Melting point 

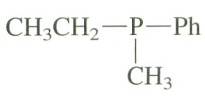
or 

**b)** Boiling point 

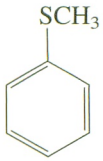

**c)** Boiling point 

or 


**12.25** What is the functional group present in these compounds?

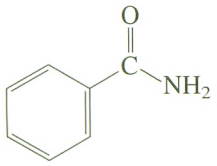
**a)** 

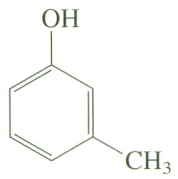

**b)**


**c)** 

**d)** $CH_3CH_2\overset{\overset{O}{\|}}{S}Ph$ **e)** $CH_3\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}CH_3$ **f)** $CH_3CH_2\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}OH$

**12.26** Identify the most acidic site in these compounds:

**a)** 

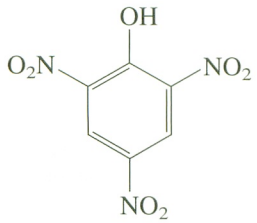
**b)** 

**c)** $CH_3\overset{\overset{O}{\|}}{C}OCH_2CH_2CH_3$

**d)** $CH_3CH_2\overset{\overset{O}{\|}}{C}CH_2CH_3$ **e)** $CH_3CH_2CH_2\overset{\overset{O}{\|}}{C}OH$

**12.27** Suggest explanations for the origins of "ibu," "pro," and "fen" in the name ibuprofen. Provide a systematic name for this compound (see page 479).

**12.28** The $pK_a$ for picric acid is 0.42. Explain why it is such a strong acid.



Picric acid

**12.29** Use Table 4.2 to find a base that is strong enough to deprotonate benzoic acid but not *p*-methylphenol. Then explain how this base might be used to separate these two compounds in the laboratory.

**12.30** The hydrogens of a hydrocarbon can be randomly replaced by chlorine by reaction of the hydrocarbon with $Cl_2$ in the presence of light. An unknown compound, **A,** with the formula $C_4H_{10}$, produces two isomeric monochlorides, **B** and **C,** with the formula $C_4H_9Cl$, when submitted to these reaction conditions. Monochloride **B** produces three isomeric dichlorides, **D, E,** and **F,** with the formula $C_4H_8Cl_2$, when submitted to these reaction conditions. Monochloride **C** gives a single dichloride, **D,** when submitted to these reaction conditions. Show the structures of **A, B, C, D, E,** and **F.** Are there any ambiguities in these structure assignments?

$$\underset{C_4H_{10}}{\mathbf{A}} + Cl_2 \xrightarrow{\text{light}} \underset{C_4H_9Cl}{\mathbf{B}} + \underset{C_4H_9Cl}{\mathbf{C}}$$

$$\mathbf{B} + Cl_2 \xrightarrow{\text{light}} \underset{C_4H_8Cl_2}{\mathbf{D}} + \underset{C_4H_8Cl_2}{\mathbf{E}} + \underset{C_4H_8Cl_2}{\mathbf{F}}$$

$$\mathbf{C} + Cl_2 \xrightarrow{\text{light}} \mathbf{D}$$

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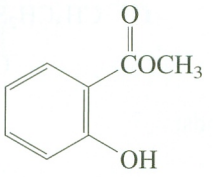
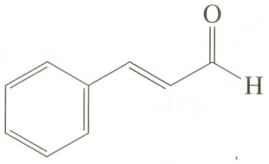
**12.31** Provide systematic names for these naturally occurring compounds:

**a)**



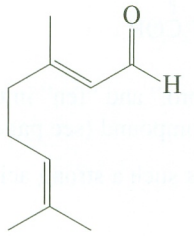

Methyl salicylate (from oil of wintergreen)

**b)**



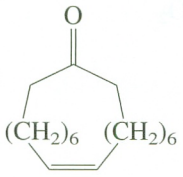

Cinnamaldehyde (from cinnamon)

**c)**



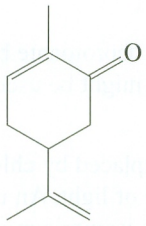

Citral (from lemons)

**d)**



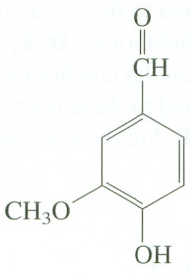

Civetone (a perfume ingredient from the civet cat) (heptadec = 17)

**e)**



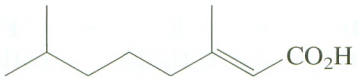

(From caraway seeds) (see problem 5.34)

**f)**

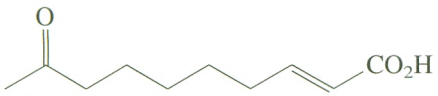



Vanillin (from vanilla beans)

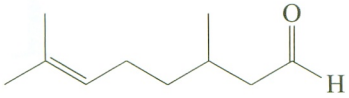
**g)**




(Sex attractant of the bean weevil)

**h)** 

Queen substance (secreted by the queen bee to prevent development of other queens)

**i)** 

(An alarm substance produced by ants)

**j)**

Oleic acid (an unsaturated fatty acid) (octadec = 18)

**12.32** Provide structures for these naturally occurring compounds:

**a)** 2,6-Diaminohexanoic acid (lysine, an amino acid)

**b)** Hex-2-en-1-yl acetate (sex attractant of Indian water bug)

**c)** (*Z*)-7-Dodecen-1-yl acetate (sex attractant of elephants and moths)

**d)** (*Z*,*Z*)-9,12-Octadecadienoic acid (linoleic acid, a polyunsaturated fatty acid) (octadec = 18)

**e)** (*all E*)-3,7-Dimethyl-9-(2,6,6-trimethylcyclohex-1-en-1-yl)nona-2,4,6,8-tetraenal (all-*trans*-retinal, or vitamin A aldehyde)

**f)** (*E*)-*N*-(4-Hydroxy-3-methoxybenzyl)-8-methyl-6-nonenamide (capsaicin, the hot ingredient in chili peppers) (benzyl is $PhCH_2$)

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## Problems Using Online Three-Dimensional Molecular Models

ORGANIC Chemistry Now™
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**12.33** Name these compounds.

**12.34** Explain which compound has the higher melting point.

**12.35** Explain which compound has the higher boiling point.

**12.36** Explain whether each compound is soluble in aqueous NaOH, aqueous $NaHCO_3$, both, or neither.

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